

12 Emulsions and Microemulsions

Emulsions are dispersions of one liquid in another in a form of droplets of the size usually between 0.1 to 10 μm . If they are between 0.01 and 0.1 μm , the systems are called microemulsions. There is a visual distinction: microemulsions are clear while (coarse) emulsions are cloudy, because of differences in light scattering.

The two phases of emulsions are immiscible or partially miscible and, as discussed in Sec. 11.4, the dispersion is stabilized by surfactants, called emulsifying agents, or emulsifier, including the stabilization by small solid particles. But it is not in equilibrium as a whole, although locally in equilibrium. In fact, emulsifiers are not only to reduce the interfacial tension but also to make emulsions behave in a complicated manner as a whole, as seen below.

The stability discussed before was against the emulsion breaking due to coalescence of the dispersed droplets at their encounter. There are other practically important phenomena of emulsions, called creaming (sedimenting or settling) and inversion. These do not, however, contribute to the phase separation, contrary to breaking. Creaming is the separation of an emulsion into a condensed and a dilute fraction due to the density difference of the droplets and the medium by centrifuging or in gravity. The condensed part is rich in the dispersed phase, like condensed milk (30 to 49% fat compared to 10% in raw whole milk). On the other hand, inversion is particularly important in preparing an emulsion of small droplets and discussed in the following section.

The practical applications of emulsions and microemulsions include dairy products, pharmaceutical preparations, cosmetics, the petroleum industry, etc.

12.1 Inversion

An interesting phenomenon with an emulsion is that in which it may change its type from an O/W (oil droplets dispersed in water) type to a W/O type, or vice versa (inversion). The final type generally depends on which type is more stable at given conditions.

First we may note how much the interfacial tension is affected by emulsifying agents. In the pure paraffin oil-water system, the interfacial tension is 41 dyn/cm,

which is reduced to 31 dyn/cm on making the aqueous phase 0.001 M in oleic acid, ending in a reasonably stable emulsion. It falls to 7.2 dyn/cm on neutralizing by 0.001 M sodium hydroxide. It becomes less than 0.01 dyn/cm if also made 0.001 M in NaCl. If we started with olive oil instead of paraffin oil, the final tension is 0.002 dyn/cm. It is small enough to make the system spontaneously emulsified without agitation. However, this statement does not refer to the emulsion type.

According to Bancroft's rule, the external (continuous) phase is that in which the emulsifying agent is the more soluble (Bancroft, 1913, 1915). In Sec. 11.4 we have learned the similar effect with stabilization by small solid particles. Bancroft introduced a concept of two interfacial tensions on both surfaces of the interfacial film of an emulsion-stabilizing surfactant, where the inner surface (facing a droplet) is the one of a higher surface tension. Since the total free energy is $(\gamma A)_{\text{outer}} + (\gamma A)_{\text{inner}}$ ($A_{\text{outer}} > A_{\text{inner}}$), where A is the area, the above arrangement can correspond to a lower free energy compared to that of the inverted arrangement (Exercise 12.1). Thus, sodium soaps tend to stabilize O/W emulsions and the relatively more oil-soluble metal soaps tend to support W/O emulsions.

If two or more solutes are present, the theoretical treatment will depend on their solubilities. If all of them are soluble, the thermodynamic treatment of Chapt. 2 may be used. In particular, an interesting situation is the mixture of two solutes: one is more soluble in water and another is more soluble in oil. In some case, the two solutes well mix each other to work as a standard of the HLB number as described in the following section. In other cases, they may behave separately (Exercise 12.2). If one of them is insoluble in both water and oil and forms a monolayer, others are adsorbed by or penetrate into the monolayer. The penetration may be measured (usually on the surface of a one-component liquid) by radioactive labeling (Hendrikx and Ter-Minassian-Saraga, 1975) or other methods (Alexander et al., 1976; Hall, 1986; Takeo, 1993). A good stabilizing effect of mixed films may lie in the very low rate at which they desorb. An important aspect is to provide a barrier to resist the coalescence of two droplets of inner phase at their encounter.

In a stable, say, O/W emulsion, what can be the maximum ratio of volumes of the oil and water component? From the above discussion on the interfacial tension, the continuous phase (water) can be a very thin film surrounding oil droplets. If the droplets are allowed to have various spherical sizes, the maximum volume ratio of oil to water can then be very large (Exercise 12.3). On the other hand, for a monodisperse emulsion, the maximum volume fraction of the oil component is geometrically 0.74 (Exercise 12.4). But, these statements do not actually represent the exact observation. In fact, continued addition of oil to an O/W emulsion can cause a change of the emulsion type, i.e., inversion at a certain volume fraction (Exercise 12.5).

The inversion can also take place by adding, say, a calcium salt to an O/W emulsion stabilized by a sodium soap, since soaps with polyvalent cations stabilize W/O emulsions. Change of temperature can result in inversion of some emulsions as discussed in the next section. An important observation is that the interfacial tension at the inversion is very low (Shinoda and Friberg, 1986).

12.2 The Hydrophile-Lipophile Balance (HLB), Factors Determining Types of Emulsion

In emulsions, empirical observation still leads theory. In practice, it is desirable to be able not only to predict the type of an emulsion but also to suggest which surfactant gives maximum stability in emulsification. An attempt at prediction was initiated by Griffin (1949, 1954) by using Bancroft's rule. He invented a way of assigning a semiempirical scale called HLB (hydrophile-lipophile balance) numbers (see Sherman, 1968; and Shinoda and Friberg, 1986) for various existing methods of assigning the HLB numbers. However, the HLB concept cannot be expected to provide information on the emulsion stability.

One method is as follows. A value of 1 is assigned arbitrarily to oleic acid (predominantly lipophilic) and a value of 20 to sodium oleate (predominantly hydrophilic). Their mixture is assumed to obey additivity. Hence, the scale (*HLB*) can be constructed for their mixture by

$$HLB = 1 \cdot W_{\text{oleic acid}} + 20 \cdot W_{\text{sodium oleate}} \quad (12.1)$$

where W is the weight fraction. This mixture is used as a reference for assigning the *HLB* number to other emulsifiers by comparing the abilities in forming a W/O or O/W emulsion out of a 50/50 mixture of white oil and water. However, this is a tedious procedure.

An easier method is to relate the *HLB* number of an emulsifier to the chemical nature of the molecule by assigning group *HLB* numbers to structural, hydrophilic and lipophilic, groups of the molecule and just adding the pertinent group *HLB* numbers and number 7 together. The group numbers assigned to specific structural groups are found in the list of Davis (1957), which appears in books on colloids such as Vold and Vold (1983). For instance, the group *HLB* numbers, -0.475 and 1.9 , are found to be assigned to chemical groups, $-\text{CH}-$ and $-\text{OH}$ (free), respectively. (Groups, CH_3- , $-\text{CH}_2-$ and $-\text{CH}-$, have the same group number of -0.475 .) Thus, the *HLB* number of cetyl alcohol, $\text{C}_{16}\text{H}_{33}\text{OH}$, can be calculated as $16(-0.475) + 1.9 + 7 = 1.3$. Also see Becher (1985) for extensive bibliographies on *HLB*.

The following is another empirical relation. Namely, for nonionic surfactant, the following simple rule is available (Shinoda and Friberg, 1986).

$$HLB = 20W_h / (W_h + W_l) \quad (12.2)$$

where W_h and W_l are molecular weights of the hydrophilic and lipophilic moieties of nonionic surfactant.

However, note that the *HLB* number of a nonionic surfactant decreases as temperature increases. This is because hydrophilic groups, which have positive group *HLB* numbers, are soluble in water due to temperature-dependent dipole-dipole interactions. The surfactant becomes less water-soluble and more oil-soluble with

increasing temperature (Exercise 12.7). Therefore, when the relative volumes of the oil and water phases are comparable, as temperature increases, the inversion from O/W to W/O occurs at a critical temperature (phase inversion temperature, *PIT*). On the other hand, the *HLB* number of an ionic surfactant alone does not change appreciably with temperature around 25°C, since ionic interactions are hardly affected by temperature.

It is interesting that there is a close correlation between the critical micellization concentration (*CMC*) (see Sec. 9.2) and the *HLB* number as follows.

$$\log CMC = a + b \log HLB \quad (12.3)$$

where a and b are constants. Note that the *HLB* value is always positive by definition. According to Eq. 9.19, *CMC* is related to the length of the hydrocarbon chain. Similarly, the *HLB* value depends on the length by the above rule.

The emulsifiers that form W/O emulsions have a low *HLB* number (3.5–6), while those that form O/W emulsions have a high *HLB* number (8–18). At inversion, the *HLB* number is between them. A good detergent has an *HLB* number between 13 to 15 and a solubilizer between 15 and 18.

The *HLB* concept is fairly satisfactory, but its major disadvantage is that it makes no allowance for temperature. In fact, an emulsion, if nonionic, can change at a certain temperature from an O/W to a W/O stabilizer or vice versa. The *HLB* number and the *PIT* are correlated.

12.3 Electrical Conductivity of an Emulsion

The electrical conductivity of an emulsion can be used to follow changes in emulsion composition and emulsion type, including inversion. If interfacial conductivity affects the emulsion conductivity, the latter will depend on the droplet size. Many emulsions, however, do not show this tendency. Therefore, a simple theory, such as the discussion of Sec. 10.7, may be used. It refers to uncharged spherical particles suspended in a conducting liquid of conductivity, σ_c . Thus, Eq. 10.99 gives the effective conductivity, σ_c^{eff} , of the emulsion:

$$\sigma_c^{\text{eff}} = \sigma_c \frac{2\sigma_c + \sigma_p - 2(\sigma_c - \sigma_p)\varphi}{2\sigma_c + \sigma_p + (\sigma_c - \sigma_p)\varphi} \quad (12.4)$$

where σ_p is the conductivity of the material of the particle and φ is the volume fraction. If the particles are charged, the electrophoresis affects the conductivity. The theoretical treatment is complicated, as mentioned in Sec. 10.7.

Since Eq. 12.4 specifies the inner (σ_p) and the outer (σ_c) conductivity, if inversion occurs by changing temperature or composition, σ_c^{eff} changes during the period of inversion. For instance, the effective specific conductivity σ_c^{eff} was mea-

sured of an aqueous solution of potassium iodide and water-saturated phenol at 19.6°C as a function of composition to detect the inversion (Manegold, 1952). The result shows a phase inversion over the range of a volume fraction of phenol between 0.55 and 0.65. Such a transition region is called the D (detergent) phase, where the emulsifier is considered to work as an universal solvent, solubilizing water and oil, leading to vanishing interfacial tension (Shinoda and Friberg, 1986; Sunder and Widom, 1987). At this phase, multiphase emulsions (W/O/W or O/W/O) have been observed. However, the formation of multiple emulsions, O/W/O or W/O/W, cannot be handled by Eq. 12.4. Detailed analysis of dielectric properties of emulsions are given by Clausse (1983).

12.4 Droplet Size Distribution and Emulsion Preparation

In Chapt. 7, it is suggested that the size distribution in a disperse system depends on the way it is produced. This is true with emulsions. Recently, careful control of the growth process has been developed, as described there.

12.4.1 Condensation under Mechanical Agitation

It has been shown by Rajagopal (1959) that a process whereby some quantity has a magnitude that is the resultant of a large number of random events will have a log-normal distribution. An emulsion prepared involving a mechanical agitation has this distribution, that is given by

$$f(a) = \frac{1}{\sigma\sqrt{2\pi}} \exp \left[-\frac{(\ln a - \langle \ln a \rangle)^2}{2\sigma^2} \right] \quad (12.5)$$

where a is the droplet radius and σ is the logarithmic standard deviation ($\sigma^2 = \langle (\ln a - \langle \ln a \rangle)^2 \rangle$) (Exercise 12.9). The function $f(a)$ is the probability of finding a droplet with radius a per unit range. This distribution gives a greater probability to the extremes in the radius, a , compared to usual Gaussian curve.

The measurement may be made by a scanning electron microscope (Lissant and Mayhan, 1973, by casting in styrene-based resin systems) or Coulter counter, etc. The distribution suggests a complexity of emulsion systems. If a mechanical agitation is used to emulsify, it needs to deform the droplet by a shear stress. Taylor (1934) expressed the deformation under shear by

$$\frac{L - B}{L + B} = \frac{Ga\eta}{2\gamma} \frac{19\eta_p + 16\eta}{16(\eta_p + \eta)} \quad (12.6)$$

where L and B are the major and minor axis of the deformed ellipsoid, respectively. G is the gradient of the shear velocity, a the radius of the sphere having the same volume as that of the droplet, η the viscosity of the dispersion medium, γ the interfacial tension, and η_p the viscosity of the dispersed or droplet medium. When the left-hand side of this equation approaches unity, the ellipsoid is stretched and small spheres are produced.

Experiments of Rumscheidt and Mason (1961, 1962), with initial droplet sizes of 0.05 to 0.2 cm, showed that the deformed shapes in agitation are sigmoid and broken to daughter drops of about 50 μm for $\eta_p \ll \eta$. But for $\eta_p \sim \eta$ they are ellipsoidal, necked around the center, and split into two similar drops plus three tiny satellite drops coming from the stretched neck. For $\eta_p \gg \eta$, the drops are ellipsoidal, but are not broken. An important conclusion guided by Eq. 12.6 is that a mechanical agitation in emulsifying, in general, has a fundamental limitation in the resulting droplet size. The agitation includes hydrodynamic turbulence and ultrasonic waves (agitation by cavitation).

12.4.2 Emulsion Polymerization

In Sec. 7.2, various methods leading to monodisperse systems are described. One of them is emulsion polymerization.

12.4.3 Phase-inversion Temperature Method

Small oil droplets can be found by emulsifying just below the phase inversion temperature (*PIT*) of the emulsifier. As the temperature is raised toward the *PIT*, the interfacial tension becomes continuously lower. This is due to Lundelius's rule, which states that any factor, such as a change of composition, concentration, or temperature, tending to decrease solubility, promotes surface activity (Exercise 12.10). When an O/W emulsion is at 2 to 4 degrees below the *PIT*, the low interfacial tension allows small droplets to form under a weak agitation. (The interfacial tension in the D phase vanishes.) The *PIT* is usually higher than room temperature. Therefore, once the fine emulsion is formed, it is cooled quickly to room temperature to obtain a stable emulsion.

As a modification of the above method, Shinoda et al. (1984) proposed a method. They noted that the D phase could be prepared at room temperature by using a mixture of suitable amounts of a hydrophilic and a lipophilic surfactant. If a hydrophilic emulsifier is further added to the system, an O/W emulsion of small droplets is obtained. If a lipophilic surfactant is added, a W/O emulsion results.

12.5 Creaming or Sedimentation

As with other disperse phenomena, the complexity arises from the importance of a variety of interparticle forces and coalescence. We have discussed (see Sec. 6.5) that, at infinite dilution, a small particle of radius a ($> \sim 1 \mu\text{m}$) moves in liquid at the Stokes terminal speed under gravity g ,

$$v_t = 2a^2(\rho_p - \rho_l)g/9\eta \quad (12.7)$$

where ρ_p and ρ_l are densities of the particle and liquid, respectively. We have noted, however, that Eq. 12.7 is obtained by using Stokes' law, $\gamma = 6\pi\eta a$ for a sphere of radius a in Eq. 6.74. The friction coefficient γ may be modified by the interfacial conditions, as given by Eq. 4.21. As discussed in Chapt. 4, it also depends on the shape of the particle (Eq. 4.22b).

The creaming speed is given by the terminal speed, Eq. 12.7. If the particle size is small the liquid cannot be considered as continuous and the Brownian motion is important.

At finite concentrations, hydrodynamic interactions can affect the creaming speed (Eq. 6.75) if dispersed particles behave like hard spheres. Non-hydrodynamic interactions among droplets either increase or decrease the sedimentation speed. For purely repulsive interactions, settling is hindered. Attractions induce aggregation, causing two or more particles to move effectively as a large kinetic unit and, thereby, increase the speed.

As noted in Sec. 6.5, if particle sizes are small, the Brownian motion or the diffusion cannot be ignored in sedimentation. By modifying Eq. 6.77, a criteria for the importance may be given by the Peclet number:

$$Pe = 2av_t/D = 8\pi a^4(\rho_p - \rho_l)g/3k_B T \quad (12.8)$$

If $Pe \ll 1$, the diffusion or the Brownian motion is important. For aqueous systems with $(\rho_p - \rho_l)/\rho_l \approx 1$, $Pe \approx 1$ for $1 \mu\text{m}$ particle. Therefore, if $a \ll 1 \mu\text{m}$, the perturbation due to the diffusion affects the sedimentation.

In industry, the creaming process is very important and desired to be well understood. For instance, consider homogenized milk. It usually has a particle size smaller than $1 \mu\text{m}$. Therefore, the Brownian motion affects the creaming speed. The average particle displacement in the direction x of the particle motion in time Δt is given by Eq. 4.3. Namely, for $\Delta t \ll 2\rho_p a^2/9\eta$ (viscous relaxation time),

$$\langle \Delta x^2 \rangle = 2(k_B T / 6\pi\eta a) \cdot \Delta t = 2D \cdot \Delta t \quad (12.9)$$

If the particle size becomes smaller, Eq. 12.7 predicts that the creaming speed is slower, while Eq. 12.9 shows that the diffusive displacement is larger. According to Eq. 12.9, the displacement of a $0.7 \mu\text{m}$ particle in water would be about

0.8 μm in 1 s at 25°C, while gravitational settling by the same particle of density 1.5 g/cm^3 in 1 s is 0.5 μm . The Brownian motion makes particles uniformly distributed, while gravity tries to introduce a concentration gradient. For particles of large ρ_p , Eq. 12.7 may be effective over the thermal effect, but there must be a sedimentation equilibrium. If many particles are involved, their Brownian displacements can be treated statistically by their diffusion with the diffusion coefficient proportional to $1/a$. Once a sedimentation equilibrium is reached, the flux due to sedimentation and the diffusive flux are equal and no further change macroscopically occurs in the distribution of particles. Therefore, we have

$$\ln \frac{n_2}{n_1} = \frac{4\pi a^3 (\rho_p - \rho_l) g (h_1 - h_2)}{3k_B T} \quad (12.10)$$

where n_1 and n_2 are number densities of particles at height h_1 and h_2 , respectively. This obeys the Boltzmann statistics. (See Exercises 12.12 and 12.14.)

Robins (1991) investigated the creaming process in a closed container by means of scattering of an ultrasonic wave. He observed the concentration distribution of particles as a function of time. The result shows an interesting feature of exhibiting three distinct spatial regions in the distribution. The top is a condensed region and the bottom a dilute region if $\rho_p < \rho_l$. The analysis of this behavior may be treated hydrodynamically as follows.

For simplicity, we assume that the system is monodisperse, consisting of small solid spherical particles of radius a ($\rho_p > \rho_l$). As it settles in a closed container, the concentration necessarily becomes non-uniform. Near the bottom region, the number density n of particles is large and the osmotic pressure Π is a complicated function of n ($\Pi \rightarrow nk_B T$ as $n \rightarrow 0$). The force acting on the particles is due to gravity \mathbf{g} and the osmotic pressure:

$$\frac{4\pi}{3} a^3 (\rho_p - \rho_l) \mathbf{g} - \frac{1}{n} \nabla \Pi(n)$$

Note that $-\nabla \Pi$ is a body force per unit volume, so that it must be divided by n to obtain the force acting on a particle. The mobility of particles in a concentrated region is expressed as $K(n)/6\pi\eta a$, where $K(n)$ is a correction to the mobility due to concentrations ($K(n) \rightarrow 1$ as $n \rightarrow 0$). Using this mobility, the flux of particles can be written as

$$n \frac{K(n)}{6\pi\eta a} \left[\frac{4\pi}{3} a^3 (\rho_p - \rho_l) \mathbf{g} - \frac{1}{n} \nabla \Pi(n) \right]$$

The sedimentation occurs in the direction of \mathbf{g} . The x axis may be chosen in this direction. Then the conservation law of the total number of particles, $\partial n / \partial t + (\partial / \partial x) \text{Flux} = 0$, leads to (Davis and Russel, 1989)

$$\frac{\partial n}{\partial t} + v_t \frac{\partial}{\partial x} [nK(n)] = \frac{D}{k_B T} \frac{\partial}{\partial x} \left[K(n) \frac{\partial}{\partial x} \Pi(n) \right] \quad (12.11)$$

where v_t is the terminal speed of an isolated particle in the liquid, given by Eq. 12.7 and $D = k_B T / 6\pi\eta a$. The initial condition is that $n(x, 0) = n_0$ and the boundary conditions are that the flux vanishes at the top and bottom of the container ($x = 0, h$).

As settling proceeds, the top becomes clear with a decreased concentration. Hence, in this region, the osmotic effect is less effective compared to the gravity effect. Equation 12.11 is reduced to

$$\frac{\partial n}{\partial t} + v_t \frac{d}{dn} [nK(n)] \frac{\partial n}{\partial x} = 0 \quad (12.12)$$

This has a general solution:

$$n(x, t) = f(x - vt), \quad \text{with} \quad v = v_t \frac{d}{dn} [nK(n)] \quad (12.13)$$

At the bottom of the container, the particle flux must vanish. Here, particles accumulate until the particle packing approaches random close packing (in volume fraction $\phi = 4\pi a^3 n / 3 \rightarrow 0.64$), where $\Pi \sim 1.85nk_B T / (0.64 - \phi)$ (Woodcock, 1981). In this limit, the osmotic force balances gravity and $\partial n / \partial t$ becomes less important. Hence,

$$\frac{\partial n}{\partial x} = \frac{v_t n [0.64 - (4\pi a^3 / 3)n]^2}{1.36D_0} \quad \text{and} \quad \frac{\partial n}{\partial t} = 0 \quad (12.14)$$

Near the top of the sediment, the concentration changes from the close packing to that of free settling state, so that the boundary from the sediment and the free settling region is sharp as experimentally observed.

Auzerais et al. (1988) numerically solved Eq. 12.11 with suitable $K(n)$ and $\Pi(n)$. The result qualitatively agrees with the observation of Robins (1991). However, almost none is known about the settling of non-spherical particles and aggregated systems.

A rough surface appearing at the top of a sediment has a fractal structure. There are models following to Gouyet (1996): random deposition, random deposition with surface diffusion, and ballistic deposition. (Vicsek (1992) classifies surface roughness in a different way.) These are characterized by the mean of the height distribution $\langle h \rangle$ and the standard deviation from the mean σ (Family, 1990).

In random deposition, the distribution of deposit heights obeys a Poisson distribution:

$$\sigma \propto \langle h \rangle^{1/2} \quad (12.15)$$

In random deposition with surface diffusion, σ depends on the linear size L of the substrate and

$$\sigma \approx L^\alpha f(\langle h \rangle / L^z) \quad (12.16)$$

where

$$f(x) \rightarrow \text{const. as } x \rightarrow \infty$$

$$f(x) \propto x^\beta \quad \text{as } x \rightarrow 0, \quad \text{where } \beta = \alpha/z$$

The fractal dimension is given by $D=d-\alpha$ (d : spatial dimension). Edwards and Wilkinson (1982), using an analytic approach, proposed that

$$\alpha = (3-d)/2, \quad \beta = (3-d)/4, \quad \text{and } z = 2 \quad (12.17)$$

The critical dimension appears at $d=3$, where some complicated corrections will be required (Vicsek, 1992).

In Ballistic deposition, depositing particles move on a straight line to the substrate and stick permanently on contact with existing deposit. For normal incidence, numerical studies lead to the results:

$$\sigma \propto L^\alpha \langle h \rangle^\beta \quad (12.18)$$

where

$$\alpha \approx 1/2 \quad \text{and} \quad \beta \approx 1/3 \quad \text{in } d = 2$$

Ballistic models involving an oblique incidence have been investigated by Ramanlal and Sander (1985). According to Meakin and Jullien (1987), the value of β slightly changes depending on the oblique angle with $\alpha=1/2$ for all angles.

Using Eqs. 12.15, 12.16, or 12.17, a deposit structure may clarify the sedimentation process by which the deposit has occurred.

Kardar et al. (1986) analytically treated the growth of a rough surface by introducing a random term in a Langevin equation.

12.6 Microemulsion

Microemulsion can be produced in several ways. One simple trick is to use 7 cm³ of household liquid detergent, 14 cm³ of white spirit, and 4 cm³ of n-pentanol (amyl alcohol) or n-butanol. They are mixed and left for several hours. A phase separation is observed and the upper oil phase becomes clear but exhibits a strong Tyndall effect. The interfacial tension is very small ($<10^{-3}$ dyne/cm), and particles

of radius about a few tens nm are spontaneously formed. Emulsions which are cloudy under visible light is called coarse emulsions. The droplet size is larger than 1 μm . The emulsions containing droplets of radius between about 100 nm and 1 μm are called miniemulsions.

The application of microemulsions is found in oil recovery. Oil in field reservoirs are first pushed out by pumping gas or water. This mechanical procedure, however, leave about 70% of the total oil in field recoverable. Much of it trapped in the small pore structure of the reservoir by capillary and viscous force. Numerous methods have been explored to recover at least some of the energy resources, the most successful one is to inject an aqueous surfactant solution with co-surfactant into an oil reservoir to solubilize remaining oil as a microemulsion.

In general a microemulsion consists of at least four components, water, oil, emulsifier, co-emulsifier such as an insoluble fatty alcohol. Schulman and Riley (1948) prepared a coarse emulsion stabilized by an ionic surfactant and then found it to convert to a clear system (microemulsion) on adding fatty-alcohol with $C_4 \sim C_{10}$ (a co-surfactant) to the emulsion. This observation seems to suggest that an ionic surfactant alone is not good enough to form *small* droplets, although it stabilizes the emulsions. The dielectric constant of water near the interfaces is much smaller than the bulk value and does not screen the ionic repulsion among the neighboring surfactant molecules on the interface. The insoluble co-surfactant contains electron donor or acceptor groups, such as hydroxyl or chloride, which allow it to partition itself between the core of the droplet and the interface. In this electronic process, the strongly adsorbed co-surfactant reduces the electrostatic repulsion among the primary emulsifier.

However, a microemulsion is also known to spontaneously form when the surface tension is very low, like in the *D* phase (see Sec. 12.3). The structure of microemulsions depends on the *HLB* value of the surfactants used (Shinoda and Friberg, 1986). In the region of the *D* phase, O/W microemulsions are formed on the hydrophilic boundary (a higher *HLB* value) and W/O microemulsions appear on the lower *HLB* side with an appearance of solubilized water inside inverted micelles (swollen micelles). When the *HLB* value is between them, the microemulsion has a bicontinuous (or tricontinuous if surfactants are included) structure of a lamellar three-phase system (water, oil, and surfactants) (Lindman et al., 1980, 1989). Surfactants form monomolecular layers between very thin oil layers and water layers or various liquid crystals (Lindblom and Rilfors, 1992). The observation is made by changing the temperature followed by a change in the *HLB* value.

At present, there are many views on microemulsions, as described above. We see that microemulsions are fundamentally different from coarse emulsions. The mechanism of the stabilization has not been well understood (Chen and Rajagopalan, 1990).

Miniemulsions may be produced by extreme comminution under high concentrations of emulsifier. This category of emulsions is subject to a strong capillary pressure effect against stabilization because of the droplet size. If the internal phase has low solubility in the medium, miniemulsions may be stabilized by the usual electrostatic or steric mechanisms. If the internal phase is slightly soluble, however, miniemulsions are subject to degradation by diffusion because of La-

palace pressures. For example, styrene is slightly water soluble. If it is homogenized in water containing a large amount of emulsifier, a miniemulsion is formed. Styrene then diffuses through the water from smaller to larger droplets (Ostwald ripening). Higuchi and Misra (1962) discovered that a small amount of a water-insoluble component, such as hexadecane, incorporated into the styrene droplet arrests the Ostwald ripening. The reason is as follows. The reduction of styrene concentration in the smaller droplet by diffusion to a larger one reduces the osmotic pressure with respect to the larger one. The difference in osmotic pressure thus created counteracts the capillary pressure. Miniemulsions of styrene and, in fact, of all monomers that are slightly soluble in water may be stabilized in this way. The thermodynamic analysis is given by Ugelstad (1978).

Exercises

- 12.1 Use the concept in Sec. 2.2.1, discuss the interfacial tension on the more wetting side of the surfactant film. Is it lower or higher compared with that on the other side?
- 12.2 Use Bancroft's rule and discuss the possible types of emulsions which result when two kinds of surfactants, one water-soluble and another oil-soluble, are in the oil-water mixture.
- 12.3 In the process of creaming, what would likely be theoretically the maximum fat percentage in the condensed part?
- 12.4 In an O/W emulsion, if it is a monodisperse of spherical shape of the same size, what would be the maximum volume fraction of the oil component? Assume that the droplets can touch each other to make a close packing.
- 12.5 Consider an O/W emulsion. If its inversion occurs on continued addition of oil, does this violate Bancroft's rule?
- 12.6 Find the *HLB* number of ethyl alcohol.
- 12.7 Why does the dipole-dipole interaction depend on temperature?
- 12.8 Use Eq. 12.4 and the change of σ_c^{eff} in inversion of O/W to W/O when the conductivities of water and oil are $2 \cdot 10^{-3}$ and $2 \cdot 10^{-4} \Omega^{-1} \text{cm}^{-1}$, respectively, and $\phi = 0.5$.
- 12.9 Show that Eq. 12.5 is Gaussian function of $\ln a$. If we denote by $\langle a \rangle_g$ the geometric mean of a_i ($i=1, 2, 3, \dots, N$), then show that $\langle \ln a \rangle = \ln \langle a \rangle_g$. Remark: $\langle a \rangle_g = \{\prod_i a_i\}^{1/N}$.
- 12.10 How does Lundelius' rule suggest a behavior of the interfacial tension, when the temperature of the emulsion change?
- 12.11 Why does the commercially available homogenized milk not settle for a long time?
- 12.12 Derive Eq. 12.10 from the condition of the sedimentation equilibrium.
- 12.13 Establish Eq. 12.11.
- 12.14 Derive Eq. 12.10 from Eq. 12.11 by making suitable approximations.
- 12.15 In the bicontinuous (or tricontinuous) structure of microemulsions, the lamellar form seems to be more prevalent instead of thread-like or bar-like. Is there any reason for the appearance?

References

- Alexander, D.M., Barnes, G.T., McGregor, M.A., and Walker, K., in "Phenomena in Mixed Surfactant Systems", ed. Scamehorn, J.F., ACS Symposium Series 311, ACS, Washington DC (1976).
- Auzerais, F.M., Jackson, R., and Russel, W.B., *J. Fluid Mech.* 195, 437 (1988).
- Bancroft, W.D., *J. Phys. Chem.* 17, 501 (1913); 19, 275 (1915).
- Becher, P., ed., "Encyclopedia of Emulsion Technology, Vol. 2, Application", Dekker, New York (1985).
- Chen, S.H. and Rajagopalan, R., "Micellar Solutions and Microemulsion", Springer, Heidelberg (1990).
- Clausse, M., in "Encyclopedia of Emulsion Technology", Vol. 1, ed., Becher, P., Dekker, New York (1983), p. 481.
- Davis, J.T., "Proc. 2nd Int. Congr. Surf. Act.", Vol. 1, London (1957).
- Davis, K.E. and Russel, W.B., *Phys. Fluids A* 1, 82 (1989).
- Edwards, S.F. and Wilkinson, D.R., *Proc. Royal Soc. London A* 381, 17 (1982).
- Family, F., *Physica A* 168, 561 (1990).
- Gouyet, J.F., "Physics and Fractal Structures", Masson, Springer-Verlag, Paris (1996).
- Griffin, W.C., *J. Soc. Cosmet. Chem.* 1, 311 (1949); 5, 249 (1954).
- Hall, D.G., *Langmuir* 2, 809 (1986).
- Hendriks, Y. and Ter-Minassian-Saraga, L., *CR* 269, 880 (1969); *Adv. Chem.* 144, 177 (1975).
- Higuchi, W.I. and Misra, J., *J. Pharm. Sci.* 51, 459 (1962).
- Kardar, M., Parisi, G., and Zhang, Y.-C., *Phys. Rev. Lett.* 56, 889 (1986).
- Lindblom, G. and Rilfors, L., *Adv. Colloid Interface Sci.* 41, 101 (1992).
- Lindman, B., Kamenka, N., Kathopoulis, T.M., Brun, B., and Nilsson, P.G., *J. Phys. Chem.* 84, 2485 (1980).
- Lindman, B., Shinoda, K., Olsson, U., Anderson, D., Karlström, and Wennerström, H., *Colloids and Surfaces* 38, 205 (1989).
- Lissant, K.J. and Mayhan, K.G., *J. Colloid Interface Sci.* 42, 201 (1973).
- Manegold, E., "Emulsionen", Strassenbau, Chemie und Technik, Heidelberg (1952).
- Meakin, P. and Jullien, R., *J. Physique* 48, 1651 (1987).
- Rajagopal, E.S., *Kolloid Z.* 162, 85 (1959).
- Ramanlal, P. and Sander, L.M., *Phys. Rev. Lett.* 54, 1828 (1985).
- Robins, M.M., "Microemulsions and Emulsions in Food", eds., El-Nokaly, M. and Conell, D., American Chemical Society, Washington, DC (1991), p. 230.
- Rumscheidt, F.D. and Mason, S.G., *J. Colloid Sci.* 16, 238 (1961); 17, 270 (1962).
- Schulman, J.H. and Riley, D.P., *I. Colloid Sci.* 3, 383 (1948).
- Sherman, P., in "Emulsion Science", ed., Sherman, P., Academic Press, London (1968).
- Shinoda, K. and Friberg, S., "Emulsions and Solubilization", Wiley, New York (1986).
- Shinoda, K., Kunieda, H., Arai, T., and Saijo, H., *J. Phys. Chem.* 88, 5126 (1984).
- Sunder, G. and Widom, B., *J. Phys. Chem.* 91, 4802 (1987).
- Takeo, M., *J. Colloid Interface Sci.* 157, 291 (1993).
- Taylor, G.I., *Proc. Roy. Soc. A* 146, 501 (1934).
- Ugelstad, J., *Makromol. Chem.* 179, 815 (1978).
- Vicsek, T., "Fractal Growth Phenomena", 2nd ed., World Scientific Publ., Singapore (1992), p. 207.
- Vold, R.D. and Vold, M.J., "Colloid and Interface Chemistry", Addison-Wesley, Reading, Massachusetts (1983), p. 399.
- Woodcock, L.V., *Ann. N.Y. Acad. Sci.* 371, 274 (1981).